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Key Points:

- Mantle-derived helium detected in cold methane seeps at the Cascadia Margin can be used as tracer for deep fracture systems
- Multiple methane sources as well as mixing and oxidation processes are present at the Cascadia Margin cold seeps
- The Cascadia Margin seeps are unequivocally dominated by methane

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Mantle-Derived Helium and Multiple Methane Sources in Gas Bubbles of Cold Seeps Along the Cascadia Continental Margin

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Abstract During E/V *Nautilus* NA072 expedition, multibeam sonar surveys located over 800 individual bubble streams rising from the Cascadia Margin between the Strait of Juan de Fuca and Cape Mendocino at depths between 104 and 2,073 m. Gas bubbles were collected directly at the seafloor using gastight sampling bottles. These bubbles were consistently composed of over 99% methane with traces of carbon dioxide, oxygen, nitrogen, noble gases, and more rarely higher hydrocarbons. A common previous view was that a biogenic source was responsible for seeps from within the gas hydrate stability zone (upper limit near 500-m isobath) and a thermogenic source was responsible for seeps from the upper slope and the shelf. Higher hydrocarbons in deep seeps with a biogenic methane signature, as well as the lack of higher hydrocarbons in some shallower seeps with a thermogenic methane signature, show that the origin of the gas cannot simply be attributed to seep location on the margin. Instead, mixing and oxidation processes play an integral role. ³He/⁴He ratios at Coquille SW point to a contribution of 30% mantle helium, whereas all the other investigated sites are characterized by a crustal helium signature. Hence, the Coquille SW seeps are directly or indirectly connected to the mantle or to very young oceanic crust. The detection of mantle helium in these seeps can thus be used as a tracer for deep-reaching fracture systems and their changing pathways.

1. Introduction

Gas hydrates and gas-filled pockets present in sedimentary deposits have been recognized as large reservoirs for reduced carbon in the Earth's crust (e.g., Boswell & Collett, 2011; Gorman et al., 2002). This is particularly relevant in geological settings with high carbon input, such as continental margins. Large-scale seepage has been identified at several continental margins, such as the U.S. Atlantic margin (Skarke et al., 2014), the West Spitsbergen margin (Mau et al., 2017), the Gulf of Mexico (MacDonald et al., 1994), and the U.S. Pacific margin (Johnson et al., 2015). The subduction of the oceanic Juan de Fuca plate under the continental North American plate over a period of millions of years has accreted a large wedge of sediments and crustal fragments at the Cascadia Margin in the Eastern Pacific (Tréhu et al., 1994). Natural gas seepage from the Cascadia Margin into the ocean is widespread (Bohrmann et al., 2003; Collier & Lilley, 2005; Hautala et al., 2014; Johnson et al., 2015; Kulm et al., 1986; Riedel et al., 2018; Salmi et al., 2011; Torres et al., 2009; Tréhu et al., 2006). Numerous seismic reflection profiles across the Cascadia subduction zone reveal bottom simulating reflectors (BSRs), which represent a contrast between hydrate-containing sediment overlying sediment that contains free gas (Tréhu et al., 1995). These BSRs point to a high abundance of hydrates and free gas in the Cascadia Margin accretionary complex (Torres et al., 2009; Tréhu et al., 2004). Widely present authigenic carbonates formed by oxidation of methane point to extensive methane seepage over a long time at the Cascadia Continental Margin (Suess et al., 1999; Torres et al., 2009). Gas release to the ocean is either caused by primary venting from pockets filled with gas of biogenic or thermogenic origin (Kvenvolden & Lorensen, 2001; Schoell, 1980) or by destabilization of previously formed methane hydrates (Suess et al., 1999). Riedel et al. (2018) estimate an average methane flux rate for the Cascadia Margin to about $0.9 \text{ g-yr}^{-1} \cdot \text{m}^{-2}$. As methane enters the water column at the sediment-ocean boundary, a fraction dissolves into the local seawater while the remaining part rises up in the form of gas bubbles. If the seeps are in shallow waters, the rising bubbles can eventually reach the uppermost water column and may enter the atmosphere (McGinnis et al., 2006). Pressure, temperature, salinity, and methane mass fraction determine the stability zone of

methane hydrate. At continental margins in temperate latitudes, hydrate is stable at depths greater than 400–500 m from the ocean surface (Kvenvolden & McMenamin, 1980). Recent studies at the Cascadia Margin have shown high bubble stream densities associated with the continental shelf (<180 m) and with the upper limit of the methane hydrate stability zone (near 500-m isobath). These observations suggest that modern climate change has begun to destabilize hydrate deposits in response to warming of the ocean (Hautala et al., 2014; Johnson et al., 2015). A recent review on the interaction of climate change and methane hydrates reports that the impact of dissociating hydrates is primarily limited to ocean waters and not the atmosphere (Ruppel & Kessler, 2017).

One of the best studied gas hydrate and seep sites along the Cascadia Margin is Hydrate Ridge, a morphological high within the accretionary complex between 600- and 800-m water depth that appears to be capped by gas hydrate and shows active release of methane gas (Torres et al., 2002; Tréhu et al., 1999). Hydrate Ridge has been the focus of Ocean Drilling Project (ODP) Leg 204 and is currently connected to the Ocean Observatories Initiative (OOI) cabled network (Bohrmann et al., 2003; Tréhu et al., 2006). In addition, Hydrate Ridge has provided new insights into natural hydrate and seep systems. Methane from Hydrate Ridge gas hydrate samples were inferred to have a microbial origin (Suess et al., 1999; Winckler et al., 2002) associated with H_2S (Kastner et al., 1998; Whiticar & Hovland, 1995) or with thermogenic C_{2+} gases at high-flux hydrate sites (Milkov et al., 2005). Suess et al. (1999) also observed intense venting of gas bubble streams through the hydrate stability zone. These bubble streams are interpreted to be generated by a local three-phase equilibrium of liquid, hydrate, and gas controlled by salinity and temperature (Liu & Flemings, 2006; Smith et al., 2014). Water column chemistry along the central Oregon margin and acoustic/water column studies of bubble streams from Hydrate Ridge indicates that seep-derived methane may have an impact on the upper water column and regional surface waters in this region (Heeschen et al., 2005; Philip et al., 2016). Water column studies at Hydrate Ridge reveal two different seabed methane sources. Methane with a light, biogenic carbon isotopic signature (-63 to -66‰ PDB (Pee Dee belemnite)) was found below 480-m water depth and is attributed to venting that occurs in the presence of gas hydrate-bearing sediments at the Hydrate Ridge site. Above 480-m water depth, the carbon isotope composition of the water column methane is dominated by isotopically heavier, thermogenic methane (-56 to -28‰ PDB) from the upper slope and the shelf (Heeschen et al., 2005). A heavy carbon isotope composition (-35 to -29‰ PDB) was also reported from three shelf bubble sites investigated along the Oregon and Northern California Cascadia Margin (Collier & Lilley, 2005).

Eventhough Hydrate Ridge has been the focus of many research studies, large areas of the Cascadia continental margin and associated seep systems have remained undiscovered. Here we present the chemical and isotopic compositions of gas bubbles released from five newly discovered seep sites along the Cascadia Continental Margin collected during an E/V *Nautilus* cruise in June 2016 (Dziak et al., 2018; Embley et al., 2017; Seabrook et al., 2018). The gas bubbles were collected into special titanium alloy gas-tight sampling bottles at the seafloor by using the remotely operated vehicle (ROV) *Hercules*. We use the methane composition and the occurrence of higher hydrocarbons to determine different carbon sources along the Cascadia Continental Margin. The presence of mantle helium in the gas bubbles allows us to use the emitted seep gases as a tracer for the connection to deep reaching fracture systems.

2. Field Campaign and Site Descriptions

Expedition NA072 on the E/V *Nautilus* (operated by the Ocean Exploration Trust) in summer 2016 mapped the seafloor and the water column with the primary goal of significantly expanding knowledge of the distribution and character of methane seeps along the U.S. Cascadia Margin (Washington, Oregon, and Northern California). The survey located 855 individual methane bubble streams at water depths between 104 and 2,073 m (Figure 1; Merle & Embley, 2016). Out of the 10 sites visited during ROV dives, five were sampled for gas bubble composition (Figure 1 and Table 1).

The first gas bubble samples were obtained from a vigorous stream of bubbles at the rim of the Astoria Canyon (494-m water depth) and from a steady heavy stream of bubbles at the floor of the same canyon (849-m water depth). The rim of the Astoria Canyon was characterized by extensive bubbling, carbonate deposits, and the presence of seep fauna. The site on the canyon floor had methane hydrate exposed adjacent to the bubble stream collection site (Figure 2). The third sample site, located at midslope (1,227 m)

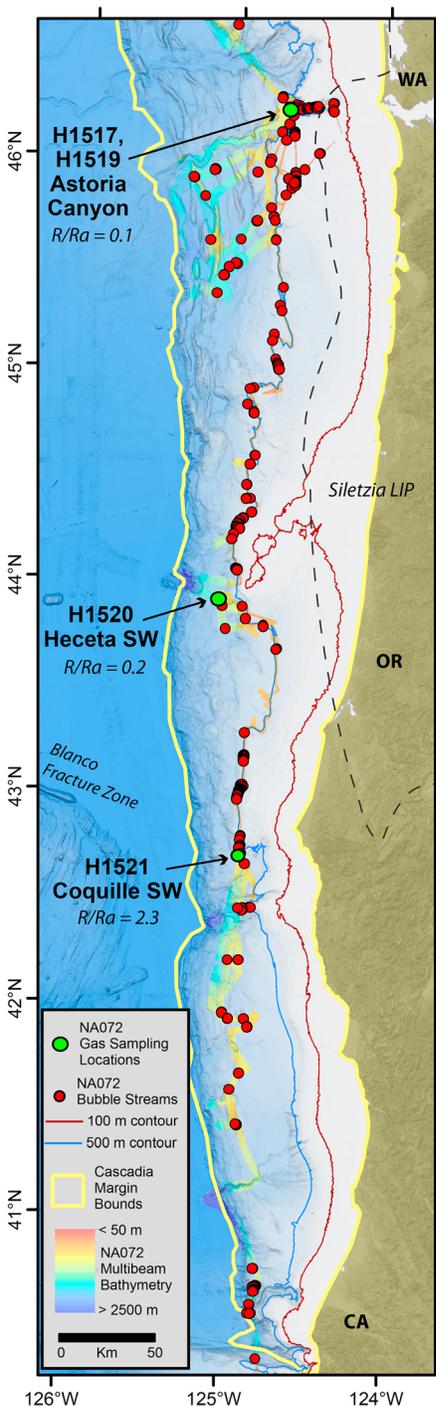


Figure 1. Bathymetry and location map of the U.S. Cascadia Margin. The map is overlaid with bubble stream locations detected during NA072 (red dots) and the ROV dive locations where gas sample were collected during NA072 (bright green dots). Bubble stream locations and bathymetry of NA072 are available in the cruise report of NA072 by Merle and Embley (2016) at <https://www.pmel.noaa.gov/eoi/pdfs/2016-PacificCoast-NA072-CruiseReport-lores.pdf>. The Siletzia large igneous province is indicated with a dashed line (data source from Wells et al., 1998). $^3\text{He}/^4\text{He}$ ratios (R/R_a) are given for each sampled site. The entire cruise track of NA072 can be found in Embley et al. (2017). Background grid courtesy of Chris Goldfinger, Oregon State University.

southwest of Heceta Bank (Heceta SW site; Figure 1), was from a large seep with a steady flow of small bubbles. At this site, small methane hydrate exposures, several bubble streams, extensive carbonate hard ground, and clam beds, tube worms, and other seep fauna were observed (Figure 2). The last two bubble samples were collected from two closely spaced bubble streams (~200 m apart) on the upper slope (615 and 619 m) southwest of Coquille Bank (Coquille SW site in Figure 1). The Coquille site had some areas with extensive steady bubbling (sample from 615 m), bubble streams with intermittent high flux bubble release (619 m), extensive carbonate deposits, and seep fauna. Evidence for shallow gas storage only centimeters below the seafloor was found when penetrating the seafloor with a probe caused gas to escape vigorously (Figure 2). No fluid flow was visible at any of the sampled sites. However, the presence of bacterial mats at all the sites is evidence for diffuse fluid flow in addition to the venting bubbles. More detailed ROV dive site descriptions and details about the seep fauna can be found in Embley et al. (2017) and Seabrook et al. (2018).

3. Sampling and Analytical Methods

Samples of gas bubbles were collected by using a funnel (funnel volumes of 350–450 mL) connected via 1/8" OD peek tubing to special titanium alloy gas-tight bottles (Edmond et al., 1992) mounted on the ROV *Hercules*. Each bottle has an internal volume of about 150 cc and was pumped to a high vacuum prior to the expedition by using the seagoing high-vacuum extraction line mounted in the Helium Isotope Laboratory of NOAA/PMEL in Newport, OR, USA. The bubble samples were collected by first holding the funnel over a bubble stream close to the seafloor and letting the funnel fill up with gas and then opening the bottle valve by depressing the bottle trigger cylinder. During bubble collection at sites located deeper than the upper limit of the hydrate stability zone (near 500 m), a thin hydrate skin formed around the bubbles in contact with the water column while the gas was accumulating in the funnel (Brewer et al., 1997). We do not expect any effect on our samples due to this hydrate formation and thus did not make any correction for this in our geochemical data set. After the expedition, the gas-tight samples were processed on the seagoing high-vacuum extraction line in the NOAA/PMEL Helium Isotope Laboratory back on shore (Lupton et al., 2006). The contents of the gas-tight bottles were dropped into the extraction line and a metal bellows pump was used to pump the released gases through a U-trap held at -60°C into a calibrated volume. The gas pressures were monitored by using precision capacitance manometers. Multiple splits of the sampled gases were then sealed into glass ampules. For total gas analysis, pyrex ampules were used, while samples for helium and neon analysis were sealed into aluminosilicate glass ampules with low helium permeability.

Helium and Ne concentrations and $^3\text{He}/^4\text{He}$ ratios were determined at the Helium Isotope Laboratory of NOAA/PMEL in Newport, OR, USA. Analysis was performed by using a 21-cm-radius, dual-collector, sector-type mass spectrometer specially designed for helium isotope analysis (Lupton, 1990). The measurements were standardized using marine air and a precisely known geothermal standard (MM gas from Yellowstone Park, 16.5 R_a) (Lupton & Evans, 2004). The precision for the helium isotope

Table 1
Sample List and Site Description of the Sampled NA072 Bubble Streams

Sample ID	Dive	Sampling Date	Site	Depth (m)	Longitude	Latitude	Hydrate Exposed	Bubble Streams
AC494	H1519	11. June 16	Astoria Canyon rim	494	−124.656	46.222	No	Vigorous
AC849	H1519	12. June 16	Astoria Canyon floor	849	−124.649	46.242	Yes	Steady, strong
HSW1227	H1520	14. June 16	Heceta SW	1227	−125.076	43.911	Yes	Steady, weak
CSW619	H1521	16. June 16	Coquille SW N	619	−124.901	42.713	No	Intermittent
CSW615	H1521	16. June 16	Coquille SW S	615	−124.901	42.711	No	Steady, strong

determination averaged 0.4% (1σ) in the $^3\text{He}/^4\text{He}$ ratio. Helium blanks averaged 1.3×10^{-10} cc STP He and the neon blanks averaged 4.7×10^{-11} cc STP Ne.

Compositional analysis of the gas samples was accomplished using gas chromatography facilities of the Lilley lab at the University of Washington in Seattle, USA. Components were separated using either Hayesep A or Hayesep Q porous polymer columns started at -50°C and ramped to 120°C . Component detection and quantification took place on a flame ionization detector and thermal conductivity detector. Standard error for CO_2 , CH_4 , and H_2 was $\pm 3\text{--}5\%$ of the measured value. Hydrocarbon analysis used the same injection manifold (known pressure, volume, and temperature of injected sample) but with diversion of the sample injection to an alternate gas chromatograph. The separation of C1–C4 components was accomplished on

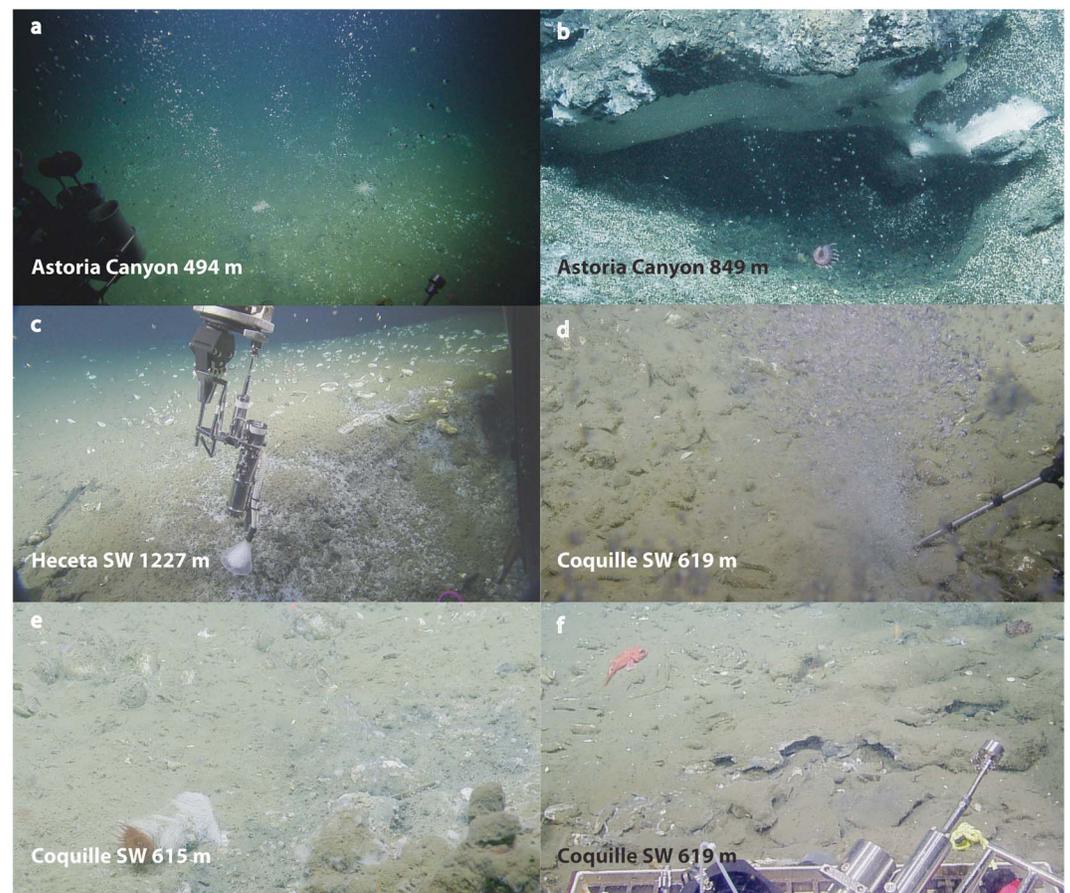


Figure 2. Photos of seep sites characterized and sampled by ROV Hercules during NA072. (a) Astoria Canyon rim at 494 m with extensive bubbling of methane. (b) Astoria Canyon floor with methane hydrate exposure and bubble streams in front at 849 m. (c) Gas bubble sampling with gas-tight sampling bottles at Heceta SW, 1,227 m. Hydrate skin is forming around the gas bubbles in contact with the water column. (d) Extensive bubbling from a gas pocket located right below the seafloor when poking it with a stick. (e) rising bubbles from the Coquille SW seep at 615-m water depth. (f) Intermittent bubbling from below carbonate hard grounds at the Coquille SW seep, 619 m.

Table 2
Chemical and Isotopic Composition of the Sampled Bubble Streams at the Cascadia Margin During NA072

Site		$\delta^{13}\text{C}_{\text{CH}_4}$ (‰)	$\delta\text{D}_{\text{CH}_4}$ (‰)	$^3\text{He}/^4\text{He}$ (R/R_a) ^a	CH_4 (%)	TCO_2 (%)	N_2 (%)	O_2 (%)	C_2H_6 (ppm)	C_3H_{6+8} (ppm)	nC_4H_{10} (ppm)	iC_4H_{10} (ppm)	$\text{CH}_4/\text{C}_{2+}$	He (ppm)	He/Ne
Astoria Canyon	AC494	-41.0	-174	0.12	99.6	0.18	0.15	0.04	28.9	0.3	0.0	0.0	34,522	4.2	548
Astoria Canyon	AC849	-65.0	-190	0.11	99.4	0.19	0.37	0.00	1.7	0.3	0.1	0.0	599,193	1.8	48
Heceta SW	HSW1227	-61.9	-192	0.18	99.4	0.32	0.20	0.00	2,251	496	73.1	186	442	3.1	247
Coquille SW	CSW619	-38.9	-176	2.35	99.5	0.24	0.17	0.01	1,212	458	4.6	13.4	821	3.1	332
Coquille SW	CSW615	-39.3	-176	2.03	98.9	0.51	0.44	0.10	1,210	339	3.2	6.5	818	3.0	149

^aHelium isotope ratio expressed as R/R_a , where $R = ^3\text{He}/^4\text{He}$ in sample and $R_a = ^3\text{He}/^4\text{He}$ in air = 1.4×10^{-6} .

micropacked columns with 1-m length of both Poropak N and Poropak S in series. Temperature programming from 35 to 125 °C of the column provided sequential elution that was quantified on a flame ionization detector. The separation of C_3H_6 and C_3H_8 was not possible with this column combination and the concentrations for these are reported as the sum. Standard error for hydrocarbons was $\pm 5\%$ of the reported values. The isotopic composition of CH_4 was determined by using a gas chromatograph interfaced with a Thermo ConFlo IV to a Thermo Delta V Plus Isotope Ratio Mass Spectrometer at the Stable Isotope Laboratory of the Geological Institute, ETH Zurich, Switzerland. Standard deviation for $\delta^{13}\text{C}$ was $\pm 0.1\%$ and for $\delta\text{D} = \pm 2.1\%$.

4. Geochemical Results

The gas composition of all sampled bubble streams are presented in Table 2. All bubble streams were dominated by CH_4 (98.9 to 99.6%) with very small percentages of CO_2 , N_2 , O_2 , C_{2+} , and helium. Hydrogen was not detected. Differences were found in the methane isotope composition as well as in the occurrence of higher hydrocarbons (C_2 to C_4). Both SW Coquille samples as well as the Heceta SW sample had elevated C_2 to C_4 concentrations, whereas the two samples from the Astoria Canyon were devoid of higher hydrocarbons. The carbon and hydrogen isotope compositions of the two deep sites, base of Astoria Canyon (849 m) and Heceta SW (1,227 m), were $\delta^{13}\text{C} = -65.0\%$ and -61.9% and $\delta\text{D} = -190$ and -192% , respectively. The shallower Astoria Canyon bubble stream at 494 m and the two Coquille SW bubble streams had a isotopic composition of $\delta^{13}\text{C} = -41.0$ to -38.9% and $\delta\text{D} = -176$ to -174% . The $^3\text{He}/^4\text{He}$ ratios of up to 2.3 R_a at both Coquille SW bubble streams indicate a significant component of mantle-derived helium. In contrast, $^3\text{He}/^4\text{He}$ ratios of 0.1 to 0.2 R_a at the other investigated sites are more consistent with a crustal He source (approximately 0.1 R_a ; e.g., Ballentine & Burnard, 2002).

5. Discussion

5.1. Multiple Methane Sources

Methane is the dominant gas ($\geq 98.9\%$) in all investigated bubble streams with only trace amounts of CO_2 , higher hydrocarbons, N_2 , and O_2 . Nitrogen and O_2 as well as some of the CO_2 are likely stripped from seawater by the bubbles. Methane seeping from continental margin sediments can have multiple origins. Gas either escapes from free gas pockets located within the sediment or is released from dissociating gas hydrate. The initial methane source, before the potential integration into hydrate, in these geological environments is typically either thermogenic decomposition of organic matter or biogenic mediation from microbial activity (Claypool & Kaplan, 1974; Schoell, 1980, 1988). A third source, abiogenic methane, has only been detected in geological settings that allow a pathway for reduced mantle carbon to the surface or where Fischer-Tropsch reactions take place in aqueous solution at elevated temperatures in presence of a metallic catalyst, such as in hydrothermal environments (Foustoukos & Seyfried, 2004; Welhan, 1988). The strong dominance of methane over higher hydrocarbons at the Cascadia Margin contrasts to gas compositions observed at the Gulf of Mexico slope (CH_4 mean = 87.7%, C_{2+} mean = 12.3%), where gas leaks from an extensive oil and gas province generated from Mesozoic source rocks beneath thick sediment layers deposited within large salt withdrawal basins (Sassen et al., 2001). The presence of higher hydrocarbons in some of the bubble streams indicates that the Cascadia Margin bubbles are at least partially influenced by thermogenic processes. The carbon and hydrogen isotope compositions of our Cascadia Margin methane bubble samples point to a

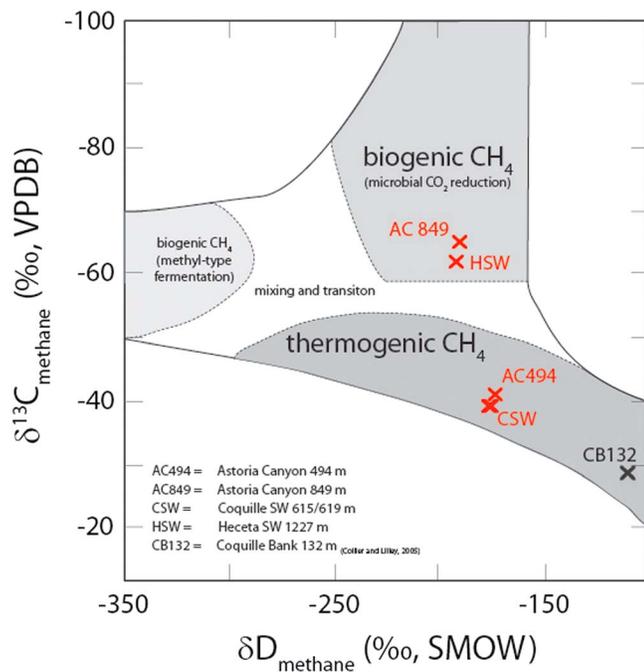


Figure 3. C versus D isotope diagram to determine the source of the methane from the Cascadia Margin seeps. Methane carbon isotopes point to a biogenic source for Heceta SW and for Astoria Canyon 849 m (microbial CO₂ reduction) and to a thermogenic source for both Coquille SW sites and for Astoria Canyon 494 m. The data point CB132 is from a shallow seep (132 m) located at the Coquille Bank published in Collier and Lilley (2005). Diagram after Whiticar (1999).

thermogenic gas source for CH₄ seeping from sediment located at 620-m or less water depth (Table 2 and Figure 3). In contrast, CH₄ released at greater water depths has a biogenic origin. A comparable pattern has been observed in a water column study above Hydrate Ridge. Heeschen et al. (2005) found that above a water depth of 480 m the methane was dominated by isotopically heavier methane ($\delta^{13}\text{C} = -40$ to -12‰), interpreted as mixtures of biogenic and thermogenic sources from the slope and upper shelf with a heavy background component. The methane isotope composition from deeper sites ($\delta^{13}\text{C} = -68$ to -42‰), where hydrate was present at the seafloor, was consistent with a solely biogenic origin (Heeschen et al., 2005). In another Cascadia Margin study, a purely thermogenic methane signature was found in bubble streams originating from the Oregon shelf at Coquille Bank at a water depth of about 130 m ($\delta^{13}\text{C} = -29\text{‰}$; Collier & Lilley, 2005). Collier and Lilley (2005) additionally observed an elevated concentration of ethane (C₂H₆) consistent with a thermogenic methane signature in the same bubble samples. The Coquille SW bubble streams at 615- and 619-m water depths reported in this study show a similar pattern, with thermogenic methane and elevated concentrations of higher hydrocarbon, such as ethane (C₂H₆), propane (C₃H₈), and butane (C₄H₁₀) consistent with a deep gas source (Table 2). In contrast, the deeper Heceta SW site (1,227 m), where exposed hydrate is present, is characterized by a biogenic methane isotope signature, but also complemented with the presence of ethane (C₂H₆), propane (C₃H₈), and butane (C₄H₁₀).

The correlation between the carbon isotope signature of methane and the ratio between methane and higher hydrocarbons is illustrated in Figure 4. This figure intends to leverage the range of chemistries observed in this study and to constrain processes and sources. The Heceta SW gas composition can be interpreted as mixed composition between thermogenic and biogenic gas sources. According to Claypool and Kvenvolden (1983), thermogenic gas formation produces CH₄ concentrations about 5 to 20 times higher than ethane concentrations. For the observed ethane concentrations at Heceta SW, 1 to 4% of the methane could be attributed to a thermogenic origin with the remaining >95% generated during biogenic processes. Nevertheless, the abundance of higher hydrocarbons at this deep site, located in the hydrate stability zone, shows that the gas phase has a significant thermogenic component. As mentioned above, gas and hydrate samples collected from within the methane hydrate stability zone in nonthermogenic basins were most often attributed to a purely biogenic origin (e.g., Ruppel & Kessler, 2017). Only Milkov et al. (2005) and Claypool et al. (2006) reported a mixed thermogenic and biogenic source for methane in hydrate samples obtained from within the hydrate stability zone at the Southern Summit at Hydrate Ridge during ODP Leg 204. They report gas and isotope compositions from headspace, void gas, and gas hydrates originating from three different sources: (1) microbial methane currently generated at shallow depths, (2) microbial methane that was first buried with and then exsolved from accreted sediments, and (3) a minor but clear thermogenic source from deeper depths. The findings of Milkov et al. (2005) and Claypool et al. (2006) as well as this study greatly extend the range of thermogenic sources from shelf depths into the deeper water of the middle and lower slopes. In contrast to our Heceta SW site, the second deep site, Astoria Canyon floor, at 849 m has a purely biogenic gas source more common for sites with exposed hydrate (Figures 3 and 4). The Astoria Canyon rim site at 494 m is characterized by a thermogenic methane isotope signature (Figure 3), as traditionally observed in upper slope and shelf bubble streams, but without the expected concomitant elevation in the higher hydrocarbon concentrations (Figure 4). Microbial methane oxidation is an important process, both within the sediments and in the water column. During bacterial consumption of methane, the heavier carbon and hydrogen isotopes get enriched in the residual methane (Whiticar, 1999). Thus, the dominance of the heavy carbon isotopes at the Astoria Canyon rim site might not originate from thermogenic decomposition of organic matter, but instead may be the result of microbial oxidation of initially biogenic methane and its associated shift in isotope composition (Figure 4). However, methane in the

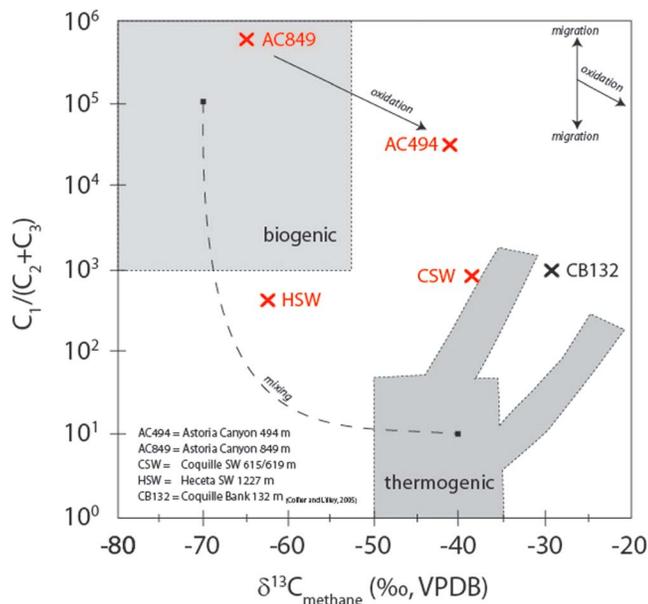


Figure 4. Simplified “Bernhard” diagram showing the concentrations of the C₁–C₃ hydrocarbon gases versus the isotopic carbon composition of methane. The Astoria 494 m (AC494) site is potentially influenced by oxidation processes. The Heceta SW seep is characterized not only by a biogenic carbon source but also by the presence of higher hydrocarbons in these gas bubbles point to a small thermogenic input. The data point CB132 is from a shallow seep (132 m) located at the Coquille Bank published in Collier and Lilley (2005). Diagram after Whiticar (1999).

gas phase is not available to microbes. Thus, it must have undergone oxidation in dissolved form within the sediments as suggested in a different study by Sahling et al. (2014) at the continental margin west of Svalbard. While oxidation of methane represents a source of dissolved inorganic carbon, no elevated CO₂ concentrations were observed in the Astoria Canyon rim bubbles. Precipitation of authigenic carbonate might have removed a substantial fraction of the generated dissolved inorganic carbon. A second possibility for an “apparent” thermogenic methane signature at the Astoria Canyon rim (without accumulation of higher hydrocarbons) is mixing between a biogenic methane source and a source dominated by heavy carbon, such as carbon from carbonate dissolution. However, no direct evidence for carbonate dissolution has been observed. Our results, even for such a limited number of sites, suggest a variation of both biogenic and thermogenic gas sources over a large depth range from the shelf to the base of the slope as well as ongoing secondary seafloor processes.

5.2. Evidence for Mantle-Derived Helium Input

The contribution of mantle ³He to a circulating fluid generates an elevated ³He/⁴He fluid signature and is known to be present in active hydrothermal venting and submarine volcanic eruptions (e.g., Baumberger et al., 2014; Lupton, 1979). In a purely sedimentary helium reservoir, no mantle ³He is present and radiogenic helium, enriched in ⁴He, is continuously produced by radioactive decay. This leads to a distinctly lower ³He/⁴He ratio in the crust than the ratio typically found in magmatic environments. The ³He/⁴He ratio is usually expressed as R/R_a, where R = ³He/⁴He in sample and R_a = ³He/⁴He in air = 1.4 × 10⁻⁶. For reference, upper mantle R/R_a = 8 and crustal R/R_a ≤ 0.1. With ³He/⁴He ratios of R = 0.1 and 0.2 R_a, our results

for the Astoria Canyon and the Heceta SW seeps are consistent with a crustal He source. A comparable ratio of 0.3 R_a was previously obtained for a gas bubble sample collected at a 132-m-deep shelf seep at Coquille Bank (Collier & Lilley, 2005). In contrast, we measured ³He/⁴He ratios of R = 2 to 2.3 R_a from the two closely spaced bubble streams at the Coquille SW site (615 and 619 m deep) in this study. These ratios indicate excess ³He consistent with a mantle He input of about 30% into the thermogenically generated gas seeping from the seafloor at Coquille SW (Figure 5). This is an unexpected finding because magmatic activity can be ruled

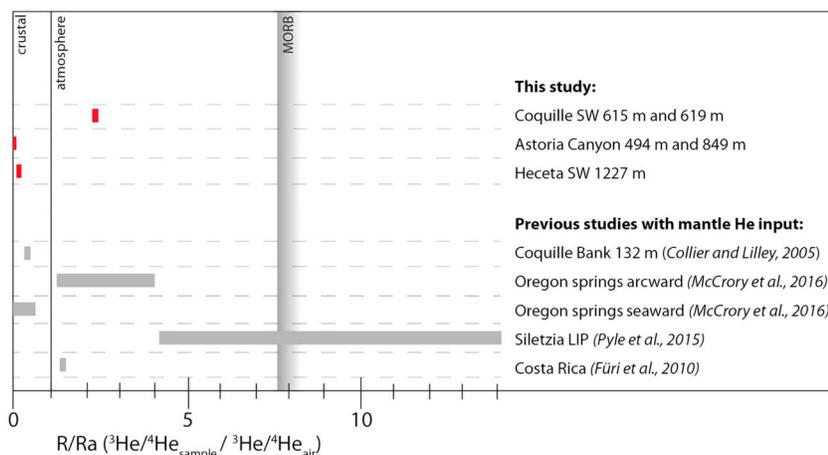


Figure 5. ³He/⁴He ratios of the sampled Cascadia Margin seeps (in red) compared with selected other forearc study sites on land and submarine with mantle he input (in gray). The ³He/⁴He ratio is usually expressed as R/R_a, where R = ³He/⁴He in sample and R_a = ³He/⁴He in air = 1.4 × 10⁻⁶. For reference, upper mantle (MORB) R/R_a = 8 and crustal R/R_a ≤ 0.1. The high ³He/⁴He ratio at Coquille SW points to a mantle contribution to the He gas of about 30% at this site. The Astoria Canyon and Heceta SW ³He/⁴He ratios point to a crustal He source.

out as a source for mantle He in this region. To date, no other instance of significant mantle He input has been found in any of the cold methane seeps along the Cascadia Margin. Mantle He input to active fluid flow has been described in other forearc regions, namely, Costa Rica (Füri et al., 2010), SW Japan (Dogon et al., 2006), New Zealand (Giggenbach et al., 1993), the Nakai Trough (Kastner et al., 1993), Alaska (Poreda et al., 1988), and the Solomon Islands (Trull et al., 1990). The helium isotope ratios of $1.3 R_a$ at the convergent margin off Costa Rica are most comparable to our findings at the Cascadia Margin. Both are submarine and located at active convergent margins associated with microplates. Their difference is found in the margin type with Cascadia being an accretionary margin and Costa Rica an erosive margin. Füri et al. (2010) reported that a potential link to oceanic igneous basement complexes or a connection to the lithospheric mantle of the downgoing slab may be responsible for the mantle helium input in the submarine forearc Costa Rica seep fluids. At the Cascadia Margin, the addition of ^3He to the Coquille SW seep could be due to (1) the serpentinized mantle wedge of the North American plate, (2) the Siletzia large igneous province (LIP) or other buried volcanic sequences, or (3) the young oceanic crust of the Juan de Fuca plate. A source from the serpentinized mantle wedge appears to be the least likely because the wedge does not extend outward to beneath the shelf edge (Tauzin et al., 2017; Tréhu et al., 1994).

Another possibility is that the fluids arise from shallower in the accretionary wedge from buried volcanic deposits. Siletzia is a large igneous province of accreted submarine and subaerial erupted lavas exposed in multiple volcanic sections of the Cascadia forearc between Vancouver Island, BC, and southern Oregon (Tréhu et al., 1994; Wells et al., 2014). The extent of the Siletzia LIP is outlined in Figure 1. Helium isotope ratios of several land-based outcrops of the Siletzia LIP range from 9.4 to $13.7 R_a$ and clearly show their magmatic origin (Pyle et al., 2015; Figure 5). If a pathway is available, residual mantle He could be extracted from these basalts through hydrothermal alteration by percolating fluids (Giggenbach et al., 1993). However, based on regional aeromagnetic data and deep exploration well records, the subsurface extent of the Siletzia LIP does not coincide with the sampling site at Coquille SW (Figure 1). A complex and extensive connecting fracture system would be needed to make the Siletzia LIP responsible for the Coquille SW He isotope ratio (Tréhu et al., 1994; Wells et al., 1998). The bubble streams sampled at Heceta SW and Astoria Canyon are located closer to the extent of the Siletzia LIP than Coquille SW, but these sites all have a crustal He isotope signature. It therefore seems unlikely that the mantle signal observed at Coquille SW is derived from the Siletzia LIP. A more likely source for the mantle He in the Coquille SW seeps is a smaller mafic ridge buried beneath the sediments of the accretionary complex from about 43° to 45°N (Fleming & Tréhu, 1999). However, if all mafic bodies or obducted parts of them were responsible for mantle He input into the Cascadia Margin seeps, it would most likely show in more bubble streams investigated at the same latitudes to date than only at the Coquille SW site.

A substantial difference between the Coquille SW seep and the sites investigated further north is the proximity of Coquille SW to young oceanic crust generated from the Gorda Ridge with accompanying internal deformation of the small Gorda plate (Wilson, 1993). At this point, with only a very limited spatial distribution of samples, the location of the mantle helium signal perhaps favors deforming young oceanic crust being subducted beneath southern Cascadia as the source of mantle helium in the Coquille SW seeps over the Siletzia LIP and other buried mafic bodies. Coquille SW is also a site of potential interaction between deeply penetrating splay faults and faults induced by intraplate deformation present on the Juan de Fuca/Gorda plate, in particular a reactivated propagator "pseudofault." The Coquille SW site is located at the edge of an area affected by such "pseudofaults," which are zones of enhanced hydration and faulting and thus potential areas of enhanced fluid flow (Horning et al., 2016; Nedimović et al., 2009; Wilson, 1989). In any case a deep penetrating fault system is required to provide access to the deep-seated source and provide a conduit to the methane seep at Coquille SW. Megasplay faults that extend upward from the subducting plate boundary megathrust to intersect the seafloor at the landward edge of the accretionary prism have been described in other subduction settings and are likely also present in the Cascadia subduction system (Moore et al., 2007). Thus, one possibility is that a recent Cascadia earthquake broke through the accreted section near Coquille Bank and is providing a delivery conduit for deep fluids from the subducting plate.

The excess ^3He Coquille SW samples are clearly anomalous compared to most measurements across continental margins. A recent study on the release of helium from the Juan de Fuca lithosphere found that springs and wells arcward of the forearc mantle corner had significantly higher ^3He input ($1.2\text{--}4.0 R_a$) than sites seaward ($0.03\text{--}0.7 R_a$) of the corner (McCroly et al., 2016; Figure 5). In contrast, our study demonstrates that high

$^3\text{He}/^4\text{He}$ ratios are also present seaward of the forearc mantle corner. Monitoring the seep gases at the Cascadia Margin for mantle helium input allows the recognition of active fluid pathways and potentially provides information about the presence of connecting fractures from the mantle to the seafloor. Helium ratios can thus potentially be used as a tracer for the dynamics of fracture systems and reactivated faults at subduction zones.

6. Conclusions

The E/V *Nautilus* NA072 expedition in summer 2016 has augmented the list of historically known bubble streams along the Cascadia Margin by more than 4 times, with new bubble streams located in water depths from 104 to 2,073 m. With only 8.6% of the total Cascadia Margin covered during this survey, a large number of sites remain to be discovered. Gas bubbles from the Cascadia Margin seeps are unequivocally dominated by over 99% CH_4 . Methane sources vary between the sites with no clear correlation with depth or location. A deep seep site with exposed hydrate in the Astoria Canyon (849 m) is releasing biogenic CH_4 , whereas bubbles from a second deep seep site with hydrate exposure, Heceta SW (1,227 m), have a mixed biogenic-thermogenic fingerprint. Similarly, the two Astoria Canyon sites, which are only separated by 2.4 km and 345 m of water depth, have different sources, with biogenic CH_4 at the deep site and an apparent thermogenic CH_4 isotopic signature at the shallower site. The lack of higher hydrocarbons at the shallower Astoria Canyon site points to ongoing seafloor oxidation processes masking the biogenic CH_4 fingerprint. The most remarkable gas composition was found at the Coquille SW seep sites at 615–619-m water depth. With a clearly thermogenic CH_4 source, the presence of excess mantle ^3He at SW Coquille demonstrates a direct or indirect connection between the cold seep and the mantle. This result raises the intriguing possibility of using ^3He , an unambiguous tracer for mantle gas input, to shed light on tectonics within the forearc and accretionary prism of subduction zones.

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